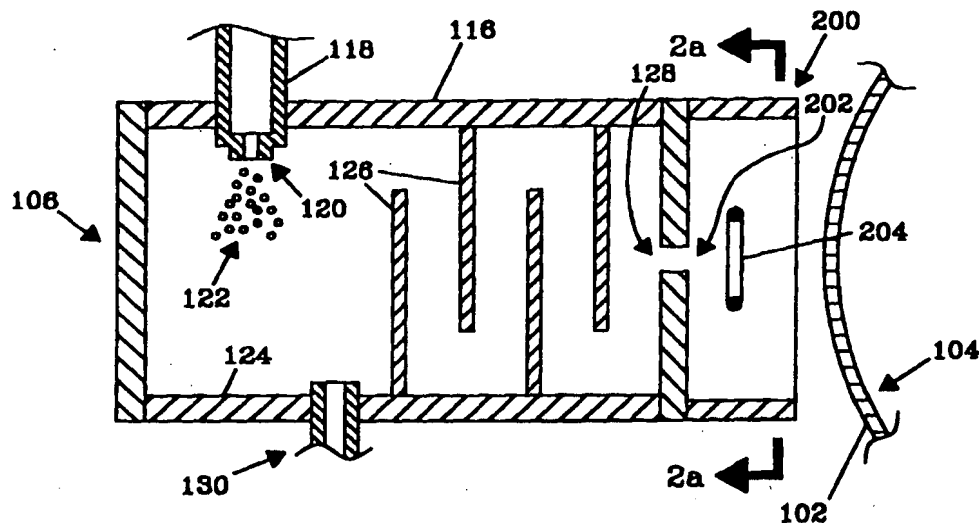




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(54) Title: PLASMA ENHANCED CHEMICAL DEPOSITION WITH LOW VAPOR PRESSURE COMPOUNDS

**(57) Abstract**

Generally, the apparatus of the present invention is (a) a flash evaporation housing (116) with a monomer atomizer (120) for making monomer particles (122), heated evaporation surface (124) for making an evaporate from the monomer particles, and an evaporate outlet (128), connected to (b) a glow discharge electrode (204) creating a glow discharge plasma from the evaporate, wherein (c) the substrate (104) is proximate the glow discharge plasma for receiving and cryocondensing the glow discharge plasma thereon. The method of the present invention has the steps of (a) flash evaporating a liquid monomer an evaporate outlet forming an evaporate; (b) passing the evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; and (c) cryocondensing the glow discharge monomer plasma on a substrate and cross-linking the glow discharge plasma thereon, wherein the cross-linking results from radicals created in the glow discharge plasma and achieves self curing.

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**PLASMA ENHANCED CHEMICAL DEPOSITION
WITH LOW VAPOR PRESSURE COMPOUNDS**

5

FIELD OF THE INVENTION

The present invention relates generally to a method of making plasma polymerized films. More specifically, the present invention relates to making a plasma polymerized film via plasma enhanced chemical deposition with a flash evaporated feed source of a low vapor pressure compound. As used herein, the term "(meth)acrylic" is defined as "acrylic or methacrylic". As used herein, the term "cryocondense" and forms thereof refers to the physical phenomenon of a phase change from a gas phase to a liquid phase upon the gas contacting a surface having a temperature lower than a dew point of the gas.

20

BACKGROUND OF THE INVENTION

The basic process of plasma enhanced chemical vapor deposition (PECVD) is described in THIN FILM PROCESSES, J.L. Vossen, W. Kern, editors, Academic Press, 1978, Part IV, Chapter IV - 1 Plasma Deposition of Inorganic Compounds, Chapter IV - 2 Glow Discharge Polymerization, herein incorporated by reference. Briefly, a glow discharge plasma is generated on an electrode that may be smooth or have pointed projections. Traditionally, a gas inlet introduces high vapor pressure monomeric gases into the plasma region wherein radicals are formed so that upon subsequent collisions with the substrate, some of the radicals in the monomers chemically bond or cross link (cure) on the substrate. The high vapor pressure monomeric gases include gases of CH_4 , SiH_4 , C_2H_6 , C_2H_2 , or gases generated from high vapor pressure liquid, for example styrene (10 torr at 87.4 °F (30.8 °C)), hexane

- 2 -

(100 torr at 60.4 °F (15.8 °C)), tetramethyldisiloxane (10 torr at 82.9 °F (28.3 °C) 1,3,-dichlorotetramethyldisiloxane) and combinations thereof that may be evaporated with mild controlled heating. Because these high vapor pressure monomeric gases do not readily cryocondense at ambient or elevated temperatures, deposition rates are low (a few tenths of micrometer/min maximum) relying on radicals chemically bonding to the surface of interest instead of cryocondensation.

Remission due to etching of the surface of interest by the plasma competes with cryocondensation. Lower vapor pressure, species have not been used in PECVD because heating the higher molecular weight monomers to a temperature sufficient to vaporize them generally causes a reaction prior to vaporization, or metering of the gas becomes difficult to control, either of which is inoperative.

The basic process of flash evaporation is described in U.S. patent 4,954,371 herein incorporated by reference. This basic process may also be referred to as polymer multi-layer (PML) flash evaporation. Briefly, a radiation polymerizable and/or cross linkable material is supplied at a temperature below a decomposition temperature and polymerization temperature of the material. The material is atomized to droplets having a droplet size ranging from about 1 to about 50 microns. An ultrasonic atomizer is generally used. The droplets are then flash vaporized, under vacuum, by contact with a heated surface above the boiling point of the material, but below the temperature which would cause pyrolysis. The vapor is cryocondensed on a substrate then radiation polymerized or cross linked as a very thin polymer layer.

The material may include a base monomer or mixture thereof, cross-linking agents and/or initiating agents.

A disadvantage of the flash evaporation is that it

- 3 -

requires two sequential steps, cryocondensation followed by curing or cross linking, that are both spatially and temporally separate.

According to the state of the art of making plasma
5 polymerized films, PECVD and flash evaporation or glow discharge plasma deposition and flash evaporation have not been used in combination. However, plasma treatment of a substrate using glow discharge plasma generator with inorganic compounds has been used in combination with
10 flash evaporation under a low pressure (vacuum) atmosphere as reported in J.D. Affinito, M.E. Gross, C.A.. Coronado, and P.M. Martin, "Vacuum Deposition Of Polymer Electrolytes On Flexible Substrates." Paper for Plenary talk in "Proceedings of the Ninth International
15 Conference on Vacuum Web Coating", November 1995 ed R. Bakish, Bakish Press 1995, pg 20-36., and as shown in FIG. 1. In that system, the plasma generator 100 is used to etch the surface 102 of a moving substrate 104 in preparation to receive the monomeric gaseous output from
20 the flash evaporation 106 that cryocondenses on the etched surface 102 and is then passed by a first curing station (not shown), for example electron beam or ultra-violet radiation, to initiate cross linking and curing. The plasma generator 100 has a housing 108 with a gas
25 inlet 110. The gas may be oxygen, nitrogen, water or an inert gas, for example argon, or combinations thereof. Internally, an electrode 112 that is smooth or having one or more pointed projections 114 produces a glow discharge and makes a plasma with the gas which etches the surface
30 102. The flash evaporator 106 has a housing 116, with a monomer inlet 118 and an atomizing nozzle 120, for example an ultrasonic atomizer. Flow through the nozzle 120 is atomized into particles or droplets 122 which strike the heated surface 124 whereupon the particles or
35 droplets 122 are flash evaporated into a gas that flows

- 4 -

past a series of baffles 126 (optional) to an outlet 128 and cryocondenses on the surface 102. Although other gas flow distribution arrangements have been used, it has been found that the baffles 126 provide adequate gas flow distribution or uniformity while permitting ease of scaling up to large surfaces 102. A curing station (not shown) is located downstream of the flash evaporator 106.

Therefore, there is a need for an apparatus and method for making plasma polymerized layers at a fast rate but that is also self curing, avoiding the need for a curing station. Such an apparatus and method would be especially useful for making PML polymer layers.

SUMMARY OF THE INVENTION

The present invention may be viewed from two points of view, viz (1) an apparatus and method for plasma enhanced chemical vapor deposition of low vapor pressure monomeric materials onto a substrate, and (2) an apparatus and method for making self-curing polymer layers, especially self-curing PML polymer layers. From both points of view, the invention is a combination of flash evaporation with plasma enhanced chemical vapor deposition (PECVD) that provides the unexpected improvements of permitting use of low vapor pressure monomer materials in a PEDVD process and provides a self curing from a flash evaporation process, at a rate surprisingly faster than standard PECVD deposition rates.

Generally, the apparatus of the present invention is (a) a flash evaporation housing with a monomer atomizer for making monomer particles, heated evaporation surface for making an evaporate from the monomer particles, and an evaporate outlet, (b) a glow discharge electrode downstream of the evaporate outlet for creating a glow discharge plasma from the evaporate, wherein

- 5 -

(c) the substrate is proximate the glow discharge plasma for receiving and cryocondensing the glow discharge plasma thereon. All components are preferably within a low pressure (vacuum) chamber.

5 The method of the present invention has the steps of
 (a) flash evaporating a liquid monomer an evaporate outlet forming an evaporate; (b) passing the evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; and

10 (c) cryocondensing the glow discharge monomer plasma on a substrate and crosslinking the glow discharge plasma thereon, wherein the crosslinking results from radicals created in the glow discharge plasma and achieves self curing.

15 It is an object of the present invention to provide an apparatus and method combining flash evaporation with glow discharge plasma deposition.

 It is an object of the present invention to provide an apparatus and method of making a self curing polymer
20 layer.

 It is another object of the present invention to provide an apparatus and method of making a self curing PML polymer layer.

 It is another object of the present invention to
25 provide an apparatus and method of PECVD deposition of low vapor pressure monomer.

 An advantage of the present invention is that it is insensitive to a direction of motion of the substrate because the deposited monomer layer is self curing. In
30 the prior art, the deposited monomer layer required a radiation curing apparatus so that the motion of the substrate had to be from the place of deposition toward the radiation apparatus. Another advantage of the present invention is that multiple layers of materials
35 may be combined. For example, as recited in U.S. patents

- 6 -

5,547,508 and 5,395,644, 5,260,095, hereby incorporated by reference, multiple polymer layers, alternating layers of polymer and metal, and other layers may be made with the present invention in the vacuum environment.

5 The subject matter of the present invention is particularly pointed out and distinctly claimed in the concluding portion of this specification. However, both the organization and method of operation, together with further advantages and objects thereof, may best be
10 understood by reference to the following detailed description in combination with the drawings wherein like reference characters refer to like elements.

BRIEF DESCRIPTION OF THE DRAWINGS

15

FIG. 1 is a cross section of a prior art combination of a glow discharge plasma generator with inorganic compounds with flash evaporation.

20 FIG. 2 is a cross section of the apparatus of the present invention of combined flash evaporation and glow discharge plasma deposition.

FIG. 2a is a cross section end view of the apparatus of the present invention.

25 FIG. 3 is a cross section of the present invention wherein the substrate is the electrode.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

30 According to the present invention, the apparatus is shown in FIG. 2. The apparatus and method of the present invention are preferably within a low pressure (vacuum) environment or chamber. Pressures preferably range from about 10^{-1} torr to 10^{-6} torr. The flash evaporator 106 has a housing 116, with a monomer inlet
35 118 and an atomizing nozzle 120. Flow through the nozzle

- 7 -

120 is atomized into particles or droplets 122 which strike the heated surface 124 whereupon the particles or droplets 122 are flash evaporated into a gas or evaporate that flows past a series of baffles 126 to an evaporate outlet 128 and cryocondenses on the surface 102. Cryocondensation on the baffles 126 and other internal surfaces is prevented by heating the baffles 126 and other surfaces to a temperature in excess of a cryocondensation temperature or dew point of the evaporate. Although other gas flow distribution arrangements have been used, it has been found that the baffles 126 provide adequate gas flow distribution or uniformity while permitting ease of scaling up to large surfaces 102. The evaporate outlet 128 directs gas toward a glow discharge electrode 204 creating a glow discharge plasma from the evaporate. In the embodiment shown in FIG. 2, the glow discharge electrode 204 is placed in a glow discharge housing 200 having an evaporate inlet 202 proximate the evaporate outlet 128. In this embodiment, the glow discharge housing 200 and the glow discharge electrode 204 are maintained at a temperature above a dew point of the evaporate. The glow discharge plasma exits the glow discharge housing 200 and cryocondenses on the surface 102 of the substrate 104. It is preferred that the substrate 104 is kept at a temperature below a dew point of the evaporate, preferably ambient temperature or cooled below ambient temperature to enhance the cryocondensation rate. In this embodiment, the substrate 104 is moving and may be non-electrically conductive, electrically conductive, or electrically biased with an impressed voltage to draw charged species from the glow discharge plasma. If the substrate 104 is electrically biased, it may even replace the electrode 204 and be, itself, the electrode which creates the glow discharge plasma from the monomer gas.

- 8 -

Substantially not electrically biased means that there is no impressed voltage although a charge may build up due to static electricity or due to interaction with the plasma.

5 A preferred shape of the glow discharge electrode 204, is shown in FIG. 2a. In this preferred embodiment, the glow discharge electrode 204 is separate from the substrate 104 and shaped so that evaporate flow from the evaporate inlet 202 substantially flows through an
10 electrode opening 206. Any electrode shape can be used to create the glow discharge, however, the preferred shape of the electrode 204 does not shadow the plasma from the evaporate issuing from the outlet 202 and its symmetry, relative to the monomer exit slit 202 and
15 substrate 104, provides uniformity of the evaporate vapor flow to the plasma across the width of the substrate while uniformity transverse to the width follows from the substrate motion.

The spacing of the electrode 204 from the substrate
20 104 is a gap or distance that permits the plasma to impinge upon the substrate. This distance that the plasma extends from the electrode will depend on the evaporate species, electrode 204/substrate 104 geometry, electrical voltage and frequency, and pressure in the
25 standard way as described in detail in ELECTRICAL DISCHARGES IN GASES, F.M. Penning, Gordon and Breach Science Publishers, 1965, and summarized in THIN FILM PROCESSES, J.L. Vossen, W. Kern, editors, Academic Press, 1978, Part II, Chapter II-1, Glow Discharge Sputter
30 Deposition, both hereby incorporated by reference.

An apparatus suitable for batch operation is shown in FIG. 3. In this embodiment, the glow discharge electrode 204 is sufficiently proximate a part 300 (substrate) that the part 300 is an extension of or part
35 of the electrode 204. Moreover, the part is below a dew

- 9 -

point to allow cryocondensation of the glow discharge plasma on the part 300 and thereby coat the part 300 with the monomer condensate and self cure into a polymer layer. Sufficiently proximate may be connected to, resting upon, in direct contact with, or separated by a gap or distance that permits the plasma to impinge upon the substrate. This distance that the plasma extends from the electrode will depend on the evaporate species, electrode 204/substrate 104 geometry, electrical voltage and frequency, and pressure in the standard way as described in ELECTRICAL DISCHARGES IN GASES, F.M. Penning, Gordon and Breach Science Publishers, 1965, hereby incorporated by reference. The substrate 300 may be stationary or moving during cryocondensation. Moving includes rotation and translation and may be employed for controlling the thickness and uniformity of the monomer layer cryocondensed thereon. Because the cryocondensation occurs rapidly, within milli-seconds to seconds, the part may be removed after coating and before it exceeds a coating temperature limit.

In operation, either as a method for plasma enhanced chemical vapor deposition of low vapor pressure monomeric materials onto a substrate, or as a method for making self-curing polymer layers (especially PML), the method of the invention has the steps of (a) flash evaporating a liquid monomer an evaporate outlet forming an evaporate; (b) passing the evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; and (c) cryocondensing the glow discharge monomer plasma on a substrate and crosslinking the glow discharge plasma thereon. The crosslinking results from radicals created in the glow discharge plasma thereby permitting self curing.

- 10 -

The flash evaporating has the steps of flowing a monomer liquid to an inlet, atomizing the monomer liquid through a nozzle and creating a plurality of monomer particles of the monomer liquid as a spray. The spray is
5 directed onto a heated evaporation surface whereupon it is evaporated and discharged through an evaporate outlet.

The liquid monomer may be any liquid monomer. However, it is preferred that the monomer material or liquid have a low vapor pressure at ambient temperatures
10 so that it will readily cryocondense. Preferably, the vapor pressure of the monomer material is less than about 10 torr at 83 °F (28.3 °C), more preferably less than about 1 torr at 83 °F (28.3 °C), and most preferably less than about 10 millitorr at 83 °F (28.3 °C). For monomers
15 of the same chemical family, monomers with low vapor pressures usually also have higher molecular weight and are more readily cryocondensable than higher vapor pressure, lower molecular weight monomers. Liquid monomer includes but is not limited to acrylic monomers,
20 for example tripropyleneglycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol monoacrylate, caprolactone acrylate, and combinations thereof; methacrylic monomers; and combinations thereof. The (meth)acrylic monomers are particularly useful in making
25 molecularly doped polymers (MDP), light emitting polymers (LEP), and light emitting electrochemical cells (LEC).

By using flash evaporation, the monomer is vaporized so quickly that reactions that generally occur from heating a liquid monomer to an evaporation
30 temperature simply do not occur. Further, control of the rate of evaporate delivery is strictly controlled by the rate of liquid monomer delivery to the inlet 118 of the flash evaporator 106.

In addition to the evaporate from the liquid
35 monomer, additional gases may be added within the flash

- 11 -

evaporator 106 through a gas inlet 130 upstream of the evaporate outlet 128, preferably between the heated surface 124 and the first baffle 126 nearest the heated surface 124. Additional gases may be organic or
5 inorganic for purposes included but not limited to ballast, reaction and combinations thereof. Ballast refers to providing sufficient molecules to keep the plasma lit in circumstances of low evaporate flow rate. Reaction refers to chemical reaction to form a compound
10 different from the evaporate. Ballast gases include but are not limited to group VIII of the periodic table, hydrogen, oxygen, nitrogen, chlorine, bromine, polyatomic gases including for example carbon dioxide, carbon monoxide, water vapor, and combinations thereof. An
15 exemplary reaction is by addition of oxygen gas to the monomer evaporate hexamethyldisiloxane to obtain silicon dioxide.

Example 1

20 An experiment was conducted to demonstrate the present invention as shown in FIG. 2 and described above. Tetraethyleneglycoldiacrylate was used as the liquid monomer. The heated surface was set at a temperature of about 650 °F (343 °C). Liquid monomer was introduced to
25 the inlet via a capillary with 0.032 inch I.D. The ultrasonic atomizer had a tip with 0.051 inch I.D. Rate of deposition of the polymer layer was 0.5 m/min for 25 micron thick polymer layer and 100 m/min for 1 micron thick polymer layer. Visual inspection of the cured
30 polymer layer did not reveal any pin holes or other flaw.

CLOSURE

While a preferred embodiment of the present invention
35 tion has been shown and described, it will be apparent to

- 12 -

those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as
5 fall within the true spirit and scope of the invention.

- 13 -

I claim:

1. An apparatus in a vacuum chamber for plasma enhanced chemical vapor deposition of low vapor pressure monomeric materials onto a substrate, comprising:

- (a) a flash evaporation housing with a monomer atomizer for making monomer particles, heated evaporation surface for making an evaporate from said monomer particles, and an evaporate outlet; and
- (b) a glow discharge electrode downstream of the evaporate outlet creating a glow discharge plasma from the evaporate; and
- (c) said substrate receiving and cryocondensing said glow discharge plasma thereon.

15

2. The apparatus as recited in claim 1, wherein the substrate is proximate the glow discharge electrode and is electrically biased with an impressed voltage.

20

3. The apparatus as recited in claim 1, wherein said glow discharge electrode is positioned within a glow discharge housing having an evaporate inlet proximate the evaporate outlet, said glow discharge housing and said glow discharge electrode maintained at a temperature above a dew point of said evaporate.

25

4. The apparatus as recited in claim 1, wherein said flash evaporation housing has opposing baffles placed between a heated surface and the evaporate outlet.

30

5. The apparatus as recited in claim 1, further comprising a gas inlet upstream of said evaporate outlet.

6. A method for plasma enhanced chemical vapor deposition of low vapor pressure monomeric materials onto

35

- 14 -

a substrate in a vacuum environment, comprising the steps of:

(a) making an evaporate by receiving a plurality of monomer particles of the low vapor pressure monomeric materials as a spray into a flash evaporation housing, evaporating said spray on an evaporation surface, and discharging an evaporate through an evaporate outlet; and

(b) making a monomer plasma from said evaporate by passing said evaporate proximate a glow discharge electrode and creating a glow discharge for making said plasma from the evaporate; and

(c) condensing said monomer plasma onto said substrate.

15

7. The method as recited in claim 6, wherein the substrate is proximate the glow discharge electrode and is electrically biased with an impressed voltage, receiving the monomer plasma cryocondensing thereon.

20

8. The method as recited in claim 6, wherein said glow discharge electrode is positioned within a glow discharge housing having an evaporate inlet proximate the evaporate outlet, said glow discharge housing and said glow discharge electrode maintained at a temperature above a dew point of said evaporate and said substrate is downstream of said monomer plasma, substantially not electrically biased with an impressed voltage, receiving the monomer plasma cryocondensing thereon.

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9. The method as recited in claim 6, wherein said monomer is selected from the group consisting of acrylic monomer, methacrylic monomer and combinations thereof.

- 15 -

10. The method as recited in claim 9, wherein said acrylic monomer is selected from the group consisting of tripropyleneglycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol monoacrylate,
5 caprolactone acrylate, and combinations thereof;

11. The method as recited in claim 6, wherein said substrate is cooled.

10 12. The method as recited in claim 6, further comprising adding an additional gas.

13. The method as recited in claim 12, wherein said additional gas is a ballast gas.

15 14. The method as recited in claim 12, wherein said gas is a reaction gas.

20 15. The method as recited in claim 14, wherein said reaction gas is oxygen gas and said evaporate includes hexamethyldisiloxane.

16. An apparatus for making self-curing polymer layers in a vacuum chamber, comprising:

25 (a) a flash evaporation housing with a monomer inlet, monomer atomizer for receiving a liquid monomer from said monomer inlet and making monomer particles, a heated evaporation surface for making an evaporate from said monomer particles, and an evaporate
30 outlet; and

(b) a glow discharge electrode downstream of the evaporate outlet creating a glow discharge plasma from the evaporate; and

(c) said substrate for receiving,
35 cryocondensing and crosslinking said glow discharge

- 16 -

plasma thereon, said crosslinking resulting from radicals created in said glow discharge plasma for self curing.

17. The apparatus as recited in claim 16, wherein
5 the substrate is proximate the glow discharge electrode and is electrically biased with an impressed voltage.

18. The apparatus as recited in claim 16, wherein
said glow discharge electrode is positioned within a glow
10 discharge housing having an evaporate inlet proximate the evaporate outlet, said glow discharge housing and said glow discharge electrode maintained at a temperature above a dew point of said evaporate.

19. The apparatus as recited in claim 16, wherein
15 said flash evaporation housing has opposing baffles placed between a heated surface and the evaporate outlet.

20. The apparatus as recited in claim 16, further
20 comprising a gas inlet.

21. A method for making self-curing polymer layers in a vacuum chamber, comprising:

(a) flash evaporating a liquid monomer an
25 evaporate outlet forming an evaporate;

(b) passing said evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; and

(c) condensing said glow discharge monomer
30 plasma on a substrate and crosslinking said glow discharge plasma thereon, said crosslinking resulting from radicals created in said glow discharge plasma for self curing.

- 17 -

22. The method as recited in claim 21, wherein the substrate is proximate the glow discharge electrode and is electrically biased with an impressed voltage, receiving the monomer plasma cryocondensing thereon.

5

23. The method as recited in claim 21, wherein said glow discharge electrode is positioned within a glow discharge housing having an evaporate inlet proximate the evaporate outlet, said glow discharge housing and said glow discharge electrode maintained at a temperature above a dew point of said evaporate and said substrate is downstream of said monomer plasma, substantially not biased with an impressed voltage, receiving the monomer plasma cryocondensing thereon.

15

24. The method as recited in claim 21, wherein said monomer is selected from the group consisting of acrylic monomer, methacrylic monomer and combinations thereof.

20

25. The method as recited in claim 24, wherein said acrylic monomer is selected from the group consisting of tripropyleneglycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol monoacrylate, caprolactone acrylate, and combinations thereof;

25

26. The method as recited in claim 21, wherein said substrate is cooled.

30

27. The method as recited in claim 21, wherein said low vapor pressure is less than about 10 torr at 83 °F (28.3 °C).

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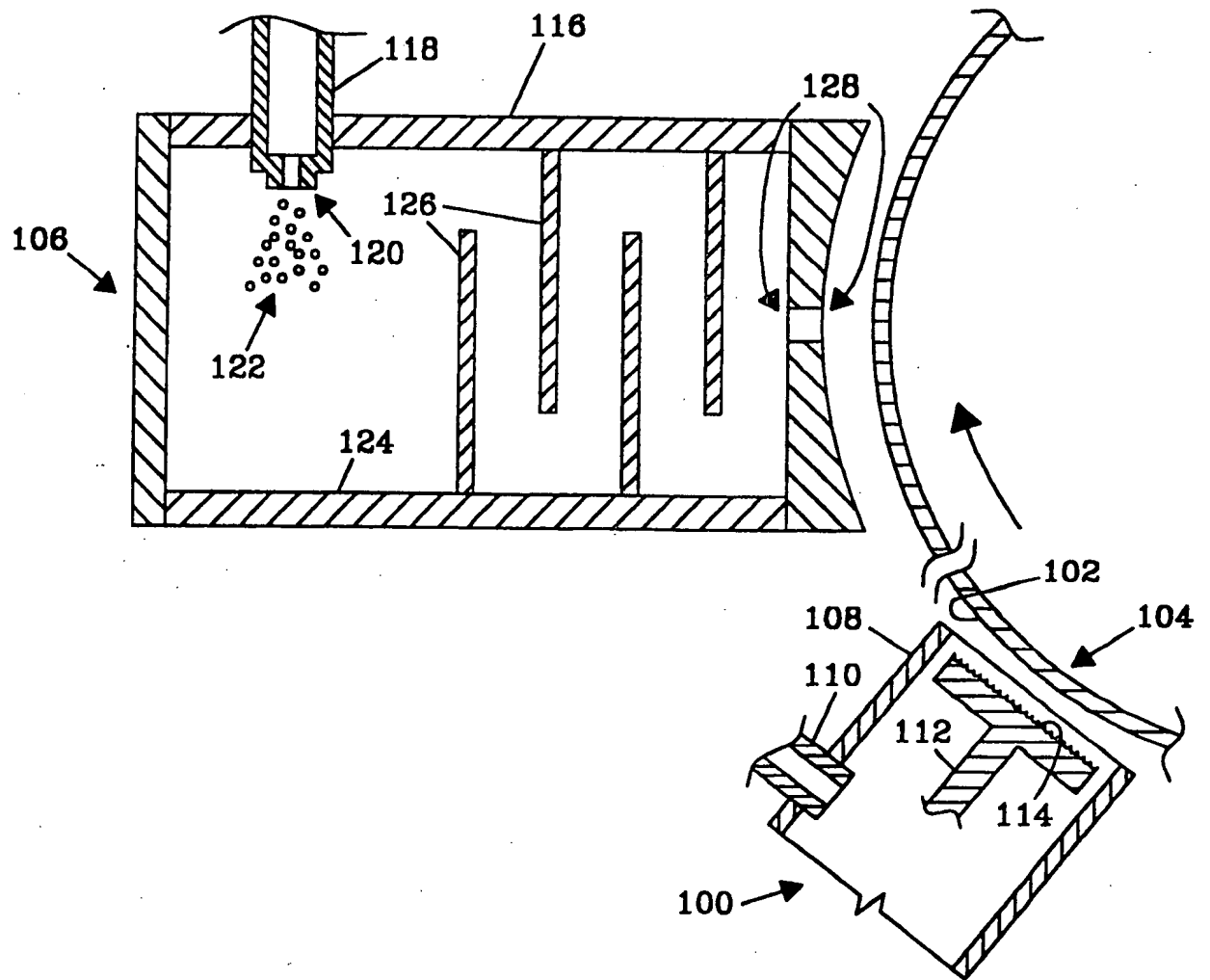
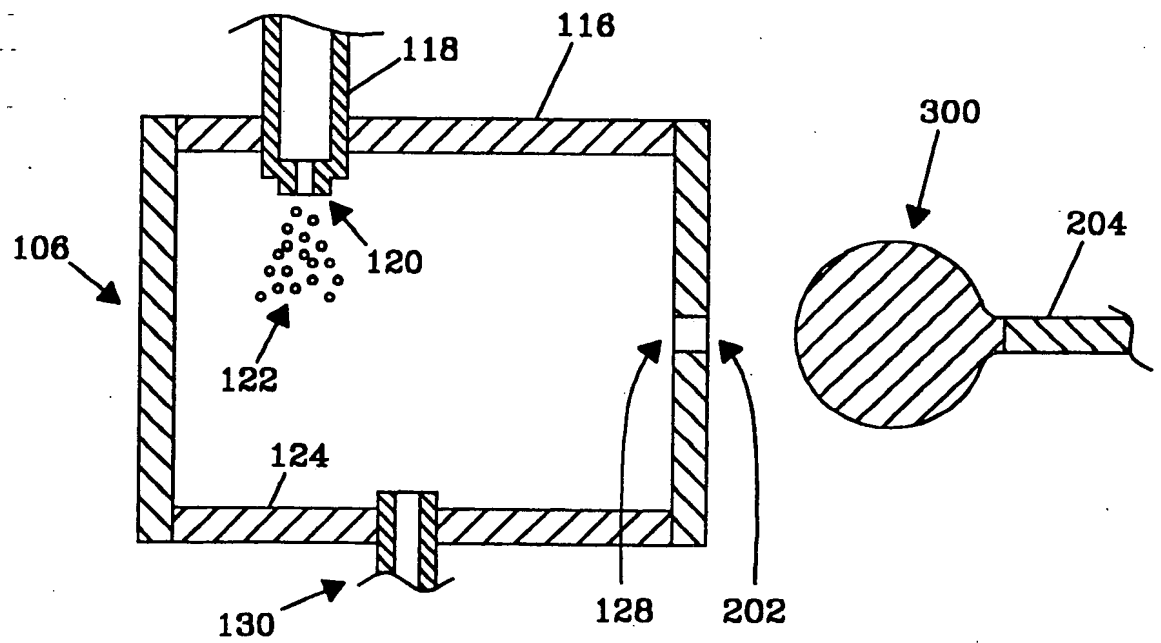


Fig. 1
(PRIOR ART)

A cross-sectional view of a device. The device consists of a central elongated component 202, an outer shell 204, and a central opening 206. The device is mounted between two vertical supports 200.

Fig. 2a

3/3

*Fig. 3*

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/20741

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C23C16/44 C23C16/50 B05D7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23C B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AFFINITO J D ET AL: "HIGH RATE VACUUM DEPOSITION OF POLYMER ELECTROLYTES" JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART A, vol. 14, no. 3, PART 01, May 1996, pages 733-738, XP000620547 see the whole document ---	1,16,21
A	US 5 032 461 A (SHAW DAVID G ET AL) 16 July 1991 see column 8, line 24 - column 13, line 10; figures 2,2A,5 ---	1,16,21
A	US 5 620 524 A (FAN CHIKO ET AL) 15 April 1997 see column 5, line 7 - line 10 see column 11, line 54 - column 13, line 20; figure 1 ---	1,16,21
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents:**

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "&" document member of the same patent family

Date of the actual completion of the international search

3 February 1999

Date of mailing of the international search report

12/02/1999

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/20741

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 299 753 A (BOC GROUP INC) 18 January 1989 see page 2, line 61 - page 4, line 65; figures 1-4</p> <p>-----</p>	<p>1,16,21</p>

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